THE CLAY MINERALOGY OF THE SHALY PORTIONS OF THE BRASSFIELD LIMESTONE

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INTRODUCTION

The Brassfield limestone outcrops over a wide area in southwestern Ohio. It shows considerable variation in physical characteristics, laterally as well as vertically.

The clay minerals associated with this formation have never been examined. It was hoped that a study of these minerals might provide additional information

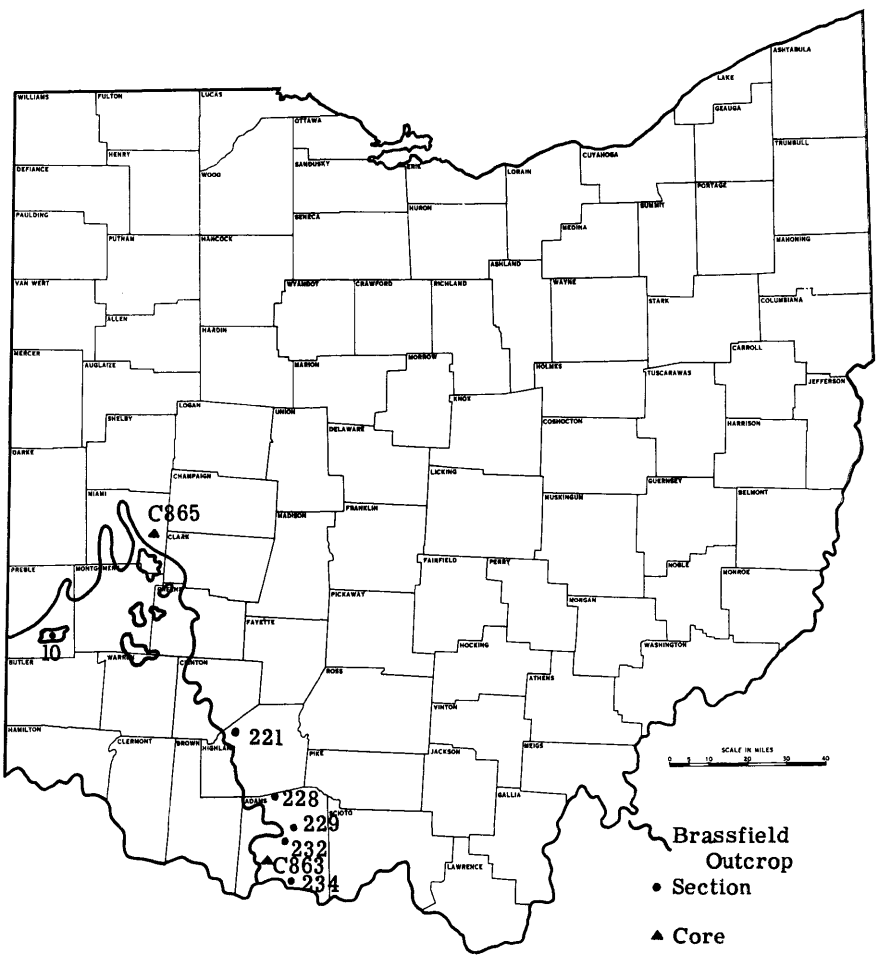


FIGURE 1. Locations of cores and stratigraphic sections.

on the variable lithology of this formation, and perhaps indicate distinctive differences among the various units.

REGIONAL GEOLOGY

The Brassfield limestone is of Silurian age and is the only formation of the Albion group which outcrops in Ohio. The area of its surface exposure is limited to southwestern Ohio (fig. 1); the outcrop area trends northeastward from the vicinity of Fairhaven, in Preble County, to central Miami County, and thence southeastward to the Ohio River near Rome, in Adams County. The outcrop area of the Brassfield limestone is divided lithologically into northern and southern zones. The boundary between these zones is a covered area in southern Clinton County.

The Brassfield formation is underlain by the Elkhorn formation, which usually consists of red and green shales, although locally it contains quartz or calcite-rich lenses. Stout (1941) reported that the Elkhorn generally contains the minerals sericite, biotite, celadonite, and hematite. Above the Brassfield lies the Dayton formation. This is commonly a bluish-gray silicious calcite-rich dolomite; locally it is a limestone.

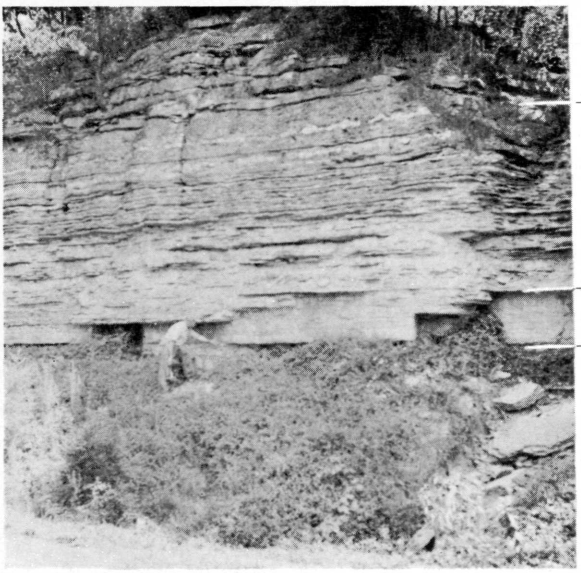


FIGURE 2. Typical Brassfield limestone section in the southern outcrop zone (locality 234).

The Brassfield formation is divided into three stratigraphic units, the Belfast (which is a transitional zone with the Elkhorn), the Lower Brassfield, and Upper Brassfield.

The Belfast unit is a greenish-gray, fine grained argillaceous dolomite or dolomitic limestone. These carbonate beds contain intercalated greenish-gray clay shales, which make up from 3 to 30 percent of the total thickness of 1 to 8 ft. Glauconite, either disseminated or in the form of pellets, is generally present. Sphalerite, pyrite, and chert are locally abundant as accessory minerals. The Belfast unit is considered to be limited to the eastern flank of the Cincinnati arch. In the western outcrop area the correlative bed is a dense limestone or argillaceous

dolomite (0.2 to 1.2 ft thick) which is occasionally present between typical Elkhorn and Lower Brassfield beds.

The Upper and Lower Brassfield units are broken into northern and southern zones by a hiatus in outcrop pattern in southern Clinton County, as well as differences in lithology.

The northern zone of the Brassfield consists of two distinct units—the Lower Brassfield and Upper Brassfield. The Lower Brassfield is typically a light gray to white, fine to coarse-grained crystalline limestone. The crystalline texture is a result of recrystallization of fossil fragments. Green clay is locally present,

TABLE 1

Analyses of the shaly portions of the Brassfield limestone

Section no.	Sample no.	Statigraphic unit	CO_3 loss with acid digestion	Analyses (in percent) $CaCO_3$	Newberry $MgCO_3$	Insoluble material
10	14A	Upper Brassfield	——	10.08	2.22	87.70
C865	2A	Dayton	35.20	——	——	64.80
"	6A	"	56.00	——	——	14.00
"	7A	"	45.00	——	——	55.00
"	10A	"	65.15	——	——	93.85
"	22A	Upper Brassfield	63.16	——	——	36.84
"	45A	Belfast	9.30	——	——	90.70
221	10	Lower Brassfield	——	3.12	0.81	96.07
228	10	" "	——	22.56	2.02	75.42
228	10A	Belfast	——	31.20	7.88	61.12
229	17A	Lower Brassfield	——	22.68	4.55	72.77
"	27A	Upper Brassfield	——	3.12	0.61	96.27
"	55A	" "	——	1.32	1.31	97.37
232	12A	Lower Brassfield	——	29.52	6.46	64.02
C863	3	Dayton	——	47.64	34.44	17.92
"	9	"	——	45.36	32.93	21.71
"	11	"	——	45.96	32.83	21.21
"	13	"	——	51.00	35.35	13.65
"	14	"	——	55.92	33.94	10.14
"	16	"	——	56.40	33.33	10.27
"	21	Upper Brassfield	——	90.72	4.44	4.84
"	22	" "	——	89.88	7.27	2.85
"	23	" "	——	91.80	4.34	3.86
"	24A	Lower Brassfield	19.20	——	——	80.80
"	27A	" "	38.24	——	——	61.76
"	28A	" "	22.00	——	——	78.00
"	30	" "	5.52	——	——	94.48
"	31A	" "	19.56	——	——	80.44
"	32A	" "	15.20	——	——	84.80
"	35A	" "	25.46	——	——	74.54
"	44A	Belfast	30.52	——	——	69.48
"	47A	"	26.52	——	——	73.48
"	48A	"	26.28	——	——	73.72
"	51	Elkhorn	24.08	——	——	75.92
234	8B	Lower Brassfield	——	27.48	6.87	65.65

either in the disseminated state or as thin partings. Bedding varies from thin to massive, with crossbedding common. Field observations indicate that the Lower Brassfield limestone is extremely dolomitic in the Clark County area; the dolomite content decreases gradually in the direction of the Indiana border. In general, the dolomite content also decreases from the bottom to the top of the unit. Pyrite is a characteristic accessory, and sphalerite is locally present in minor quantities.

The thickness of the unit varies from a minimum of 6 ft in Preble County to greater than 20 ft in Miami County.

The Upper Brassfield of the northern zone is characteristically a pink, red, or gray, medium to coarse grained bioclastic limestone. Green clay, as partings, lenses, or disseminated material is much more abundant than in the Lower Brassfield. Hematite-rich oolites and fossil fragments are present in Clinton and Greene Counties; this zone grades into a red clay in the extreme northwestern portion of Greene County. Pyrite is present as a characteristic accessory. Glauconite is occasionally present in the upper portions of the unit. The thickness varies from 1 to 22 ft and shows rapid lateral variation. The dolomite content of the Upper Brassfield parallels that of the previously described Lower Brassfield.

The Brassfield limestone of the southern zone has several features which are distinctly different from those of the northern zone. These are the following: lack of sharp lithologic differences between the upper and lower parts, a large

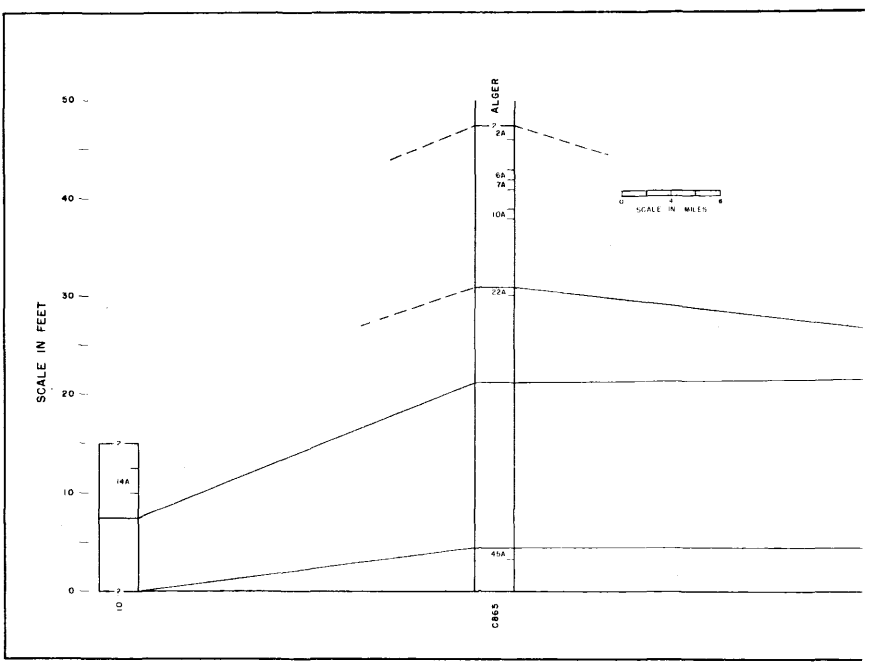


FIGURE 3. Stratigraphic sections and sample locations of the Brassfield limestone.

increase in the shale content, an increase in the number of chert nodules, and differences in many textural and structural features. Although the two rock types of the northern zone do not remain distinct in the southern zone, many of the distinguishing stratigraphic features persist, such as the ferruginous oolite zone, the basal brown limestone, and the course bioclastic texture of the Upper Brassfield.

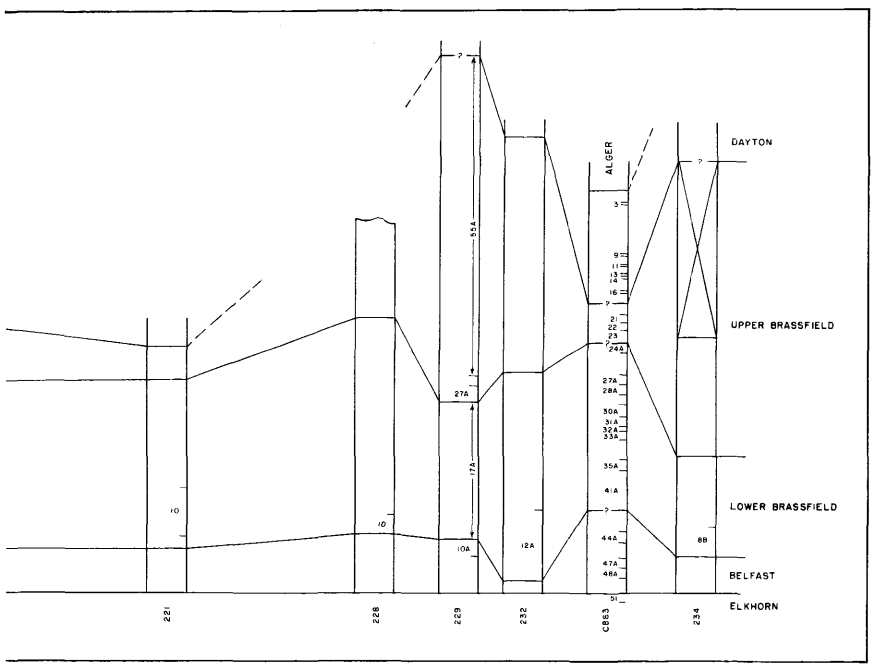
The most common rock type is a light to medium gray, fine to medium grained limestone. The interbedded green shale in some southern exposures constitutes the major portion of the unit (fig. 2), and as in the northern zone, the shale is more abundant in the upper portions. Chert, which occurs near the base, has no fixed stratigraphic position. Glauconite is fairly common throughout the unit, both as discrete beds as well as irregularly-distributed grains. Calcite is prevalent

throughout the unit, with the exception of the West Union area in Adams County, where a large proportion of dolomite is present.

PROCEDURE

Clay samples were collected from thin clay seams in limestone, from both drill cores and outcrops. The type of sample, its locality, and stratigraphic horizon are shown in figures 1 and 3.

The carbonate minerals which occur in abundance within the clay seams were removed by treatment with dilute (1: 3) glacial acetic acid; acetic acid treatment, in contrast to hydrochloric acid treatment, does not appreciably alter the clay-mineral assemblage. The samples were sieved with a 60-mesh screen, weighed, and placed in contact with acid for a minimum of 30 hr. The residue was filtered, given a triple washing with distilled water, evaporated, and reweighed. Newberry



analyses for $CaCO_3$, $MgCO_3$, and insoluble material percentages were run on most of the samples. The results are given in table 1.

Portions of each sample were mounted on glass slides for x-ray studies. Part of the sample was x-rayed by means of a Norelco low angle diffractometer. Copper radiation with a nickel filter was used. The speed was 2° 2θ per min; critical reflections were run at 1° 2θ per min. The area examined ranged from 2.31 to 22.07 Å. All of the significant clay mineral peaks, as well as those of many common impurities fall within this range.

A typical x-ray chart is shown in figure 4. The relative amounts of kaolinite and illite were determined on the basis of intensities of (001) reflections, as suggested by Murray (1953). This technique yields approximate differences in the form of a ratio, but the results are not quantitative.

All of the samples were treated with ethylene glycol in order to determine the presence of montmorillonite, and to observe the nature of the mixed-layer structures. In addition, all samples were rerun after being fired for one hr at 600° C in order to distinguish between chlorite and other clay minerals, as well as to observe effects on mixed-layer structures.

The results of the x-ray analysis are given in table 2.

DISCUSSION OF RESULTS

Comparison of the Newberry analysis in table 1 with the sample locations clearly shows that the samples collected in the southern zone are richer in insoluble material (mainly clays) than those of the northern zone. It is also interesting to note, when comparing these analyses with the clay-mineral determinations, that

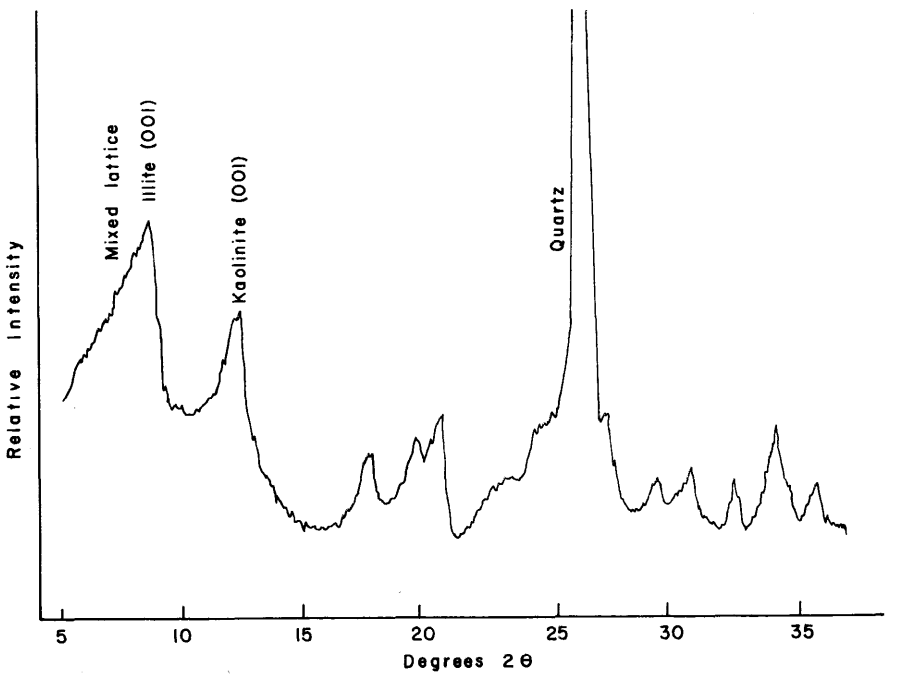


FIGURE 4. Typical x-ray diffractometer pattern (Cu radiation) of a shaly portion of the Brassfield limestone.

the composition of the clays is virtually the same, whether the sample was collected in a clay-rich band, or in a section with a high carbonate content.

As can be noted from table 2, most of the samples collected in the southern part of the outcrop region contain illite and mixed-layer illite-chlorite as the predominant clay minerals, with lesser amounts of kaolinite, and occasional traces of chlorite. The more northern samples contain a similar suite, with the difference that the kaolinite is either absent or present in only trace amounts.

These results are in agreement with similar clay-mineral studies by other investigators. Studies on the clay minerals associated with limestones and dolomites, such as those of Grim, Lamar, and Bradley (1937), Millot (1949), Grim (1951), and Robbins and Keller (1952), indicate that illite is the predominant clay mineral associated with carbonate rocks. Weaver (1958), in summarizing

much of the work done on clay minerals, concluded that although this relationship is correct, illite is also the predominant clay mineral in all sediments and is not noticeably more abundant in limestones than in shales. In most cases where shales and limestones are interbedded, they contain the same type of clay minerals.

Treatment of all samples with ethylene glycol failed to reveal the presence of montmorillonite.

It can be seen from figure 4 that the 10 Å illite peak is noticeably skewed in the direction of the wider spacings. This is often indicative of mixed-layer clay

TABLE 2

Mineral composition of the shaly portions of the Brassfield limestone

Sample number	Illite: kaolinite ratio	Other minerals	Stratigraphic unit
10–14A	Ill., Tr. Kaol.	———	Upper Brassfield
C865–2A	Ill., Tr. Kaol.	———	Dayton
C865–6A	Ill., no Kaol.	Pyr.	"
C865–7A	Ill., no Kaol.	Felds.	"
C865–10A	Ill., no Kaol.	Felds.	"
C865–22A	Ill., no Kaol.	Ill.-Ch.	Upper Brassfield
C865–45A	Ill., Tr. Kaol.	Ill.-Ch., Felds., Pyr.	Belfast
221–10	7	Ill.-Ch., Felds.	Lower Brassfield
228–10	4	Ill.-Ch., Tr. Ch.	" "
229–10A	6	Felds., Tr. Pyr.	Belfast
220–17A	3	Ill.-Ch.	Lower Brassfield
229–27A	6	Ch.	Upper Brassfield
229–55A	5	———	" "
232–12A	3	Ill.-Ch.	Lower Brassfield
C863–3	20	Tr. Ch.	Dayton
C863–9	8	Ill.-Ch.	"
C863–11	12	Ill.-Ch.	"
C863–13	Ill., no Kaol.	Ill.-Ch.	"
C863–14	4	Ill.-Ch.	"
C863–16	13	Tr. Ch.	"
C863–21	13	———	Upper Brassfield
C863–22	11	Ill.-Ch.	" "
C863–23	8	Tr. Ch.	" "
C863–24A	9	Tr. Ch.	Lower Brassfield
C863–27A	7	Tr. Ch.	" "
C863–28A	5	Tr. Ch., Felds.	" "
C863–30A	14	Ill.-Ch., Tr. Ch.	" "
C863–31A	13	———	" "
C863–32A	17	Pyr.	" "
C863–33A	24	———	" "
C863–35A–41A	8	Tr. Ch., Pyr., Felds.	" "
C863–44A	5	Ch.	Belfast
C863–47A	5	Tr. Ch., Pyr.	"
C863–48A	5	Tr. Ch.	"
C863–51	6	Ch.	Elkhorn

Quartz is present in all samples.

Ch. = Chlorite, Felds. = Feldspar, Ill.-Ch. = Illite-chlorite mixed-layer structure, Kaol. = Kaolinite, Pyr. = Pyrite, Tr. = Trace, and Ill. = Illite.

structures. A mixed-layer clay is derived from stripping or degradation of pre-existing clay minerals during weathering; cations removed from the clay structure during weathering are commonly replaced by others, either in the source area or in the basin of deposition, to form a mixed-layer structure. Treatment by ethylene glycol did not produce any broadening or shifting in the peak, indicating that the mixed-layer structure did not contain a clay with an expandable lattice. The shape of the peak either increased in skewness after firing or there was a general increase

in background between 13.8 and 10.5 Å, which is indicative of chlorite in mixed-layer arrangement with illite. This increase in intensity would be expected, as the firing of chlorite minerals which are not in a mixed-layer arrangement increases the intensity of the (001) reflection, as well as depressing the higher order reflections. The increase in intensity over such wide spacings indicates a very random arrangement of Mg or Fe within the structure. Although illite is often in mixed-layer arrangement with montmorillonite, an illite-chlorite mixed-layer structure is relatively uncommon.

The general distribution of illite to kaolinite shows the presence of kaolinite in the southern samples, and either none or merely trace amounts in the northern samples. This relationship appears to hold true for the Dayton formation, and the Upper Brassfield, Lower Brassfield, and Belfast units. Although only a relatively small number of samples have been taken, the consistency of this relationship would indicate that the clay mineralogy does differ in these two areas. Weaver (1958) states that kaolinite tends to be most common in continental and near-shore sediments. It is thus possible that the presence of kaolinite in the southern samples may indicate that this area is closer to the sediment source than the northern samples. This would be in agreement with the much greater abundance of clay in the southern samples.

No significant differences are present in outcrop samples as compared to core samples. For the most part the same clay mineralogy exists among the samples collected from the Dayton, Brassfield, and Belfast units.

CONCLUSIONS

Clay-mineral analyses were conducted on the shaly portions of the Brassfield and adjacent limestones. The predominant clay mineral is illite. Kaolinite, mixed-layer illite-chlorite, as well as trace amounts fo chlorite, were also determined. The results indicate that the more northern samples contain either traces of kaolinite or none at all, whereas those in the south usually contain significant amounts.

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